Regular Article

Arsenate removal with 3-mercaptopropanoic acid-coated superparamagnetic iron oxide nanoparticles

D. Morillo [a,*], A. Uheida [b], G. Pérez [a], M. Muhammed [b], M. Valiente [a]

[a] Universitat Autònoma de Barcelona, Centre GTS, Department of Chemistry, 08193 Bellaterra (Barcelona), Spain
[b] Royal Institute of Technology (KTH), Functional Materials Division, 16440 Kista (Stockholm), Sweden

A B S T R A C T

In the present work, superparamagnetic iron oxide nanoparticles (SPION) surface-coated with 3-mercaptopropanoic acid (3-MPA) were prepared and their feasibility for the removal of arsenate from dilute aqueous solutions was demonstrated. The synthesized 3-MPA-coated SPION was characterized using transmission electron microscopy (TEM), thermogravimetric analysis (TGA) and Fourier transform infra-red spectrometry (FTIR). Separation efficiency of the coated nanoparticles and the equilibrium isotherm of arsenate adsorption were investigated. The obtained results reveal the arsenate adsorption to be highly pH-dependent, and the maximum adsorption was attained in less than 60 min. The resulting increase of 3-MPA-coated SPION adsorption capacity to twice the adsorption capacity of SPION alone under the same conditions is attributed to the increase of active adsorption sites. An adsorption reaction is proposed. On the other hand, efficient recovery of arsenate from the loaded nanoparticles was achieved using nitric acid (HNO_3) solution, which also provides a concentration over the original arsenate solution.

© 2014 Elsevier Inc. All rights reserved.

1. Introduction

Arsenic is a relatively scarce element in the environment atmosphere, water, soil and organisms. Usually it exists combined with other elements, for example, with sulphur, oxygen and iron and the arsenic species toxicity depends on its oxidation state, being As(-III) the most toxic specie [1]. The World Health Organization (WHO) has reduced the Maximum Contamination Level (MCL) from 50 μg/L to 10 μg/L. Therefore, it is noteworthy that the continuous regulations strengthening make necessary the improvement of existing arsenic remediation methods [2,3].

A great variety of water treatment methodologies s such as precipitation [4], oxidation [5], liquid–liquid extraction [6,7], ion exchange [8], membrane processes [9], surface complexation [10] and selective adsorption [11,12] have been studied for significant reduction or remove arsenic from contaminated effluents.

The essence of nanoscience and nanotechnology is the ability to create materials, structures and systems which exhibit new properties for novel applications, a combination of the desired properties and functionalities is achieved at nanometer scale [13]. Small size gives nanoparticles a high surface area to volume ratio, a high surface reactivity, new properties such as magnetic and chemical. In this sense, the interaction with different kinds of chemical species offers better kinetics for selective sorption of ions from aqueous solutions [14]. Highly reactive nanoparticles such as nanosized sorbents have been developed specifically to remediate contamination by heavy metal ion contaminants [15,16]. Nanoparticles (10–500 nm) provide an opportunity to deliver these remedial agents to subsurface contaminants in situ, and provide access to contamination trapped in the smallest pores in an aquifer matrix.

At the nanoscale, inorganic metal oxides are potentially highly efficient agents for binding ions such as arsenic or some pollutants and today's challenge is the translation of these achievements into an industrial production environment which requires scale-up to a continuous and safe nanoparticle manufacturing process as reported elsewhere [17–19]. By tailoring the composition of the metal oxides, selective adsorption of different ions can be introduced. The utilization of nanoparticles for the recovery of metal ions from industrial wastes or natural water effluents has proved itself as superior new process.

In the present study the feasibility of using SPION coated with 3-mercaptopropionic acid is demonstrated for selective sorption of arsenate from aqueous solutions and an adsorption mechanism has been proposed as the most suitable considering the obtained results throughout the study. The sorption properties were studied under static mode of operation.

* Corresponding author.
E-mail addresses: Diego.morillo.martin@gmail.com (D. Morillo), salam@kth.se (A. Uheida), Gustavo.perez@uab.es (G. Pérez), mamoun@kth.se (M. Muhammed), manuel.valiente@uab.cat (M. Valiente).

2. Experimental section

2.1. Chemicals and reagents

Stock solutions of As(V) were prepared from $Na_2HAsO_4 \cdot 7H_2O$ (Sigma–Aldrich). Analytical grade $FeCl_2 \cdot 4H_2O$, $FeCl_3 \cdot 6H_2O$ (Sigma–Aldrich), ammonium hydroxide, toluene, sodium acetate trihydrate, acetic acid, nitric acid and sodium hydroxide were used as received. $Cu(NO_3)_2$, $Ni(NO_3)_2$, $Zn(NO_3)_2$, NH_4Cl, $NH_4(NO_3)$, $K_2(SO_4)$ and $NaH_2(PO_4)$ (Sigma–Aldrich) were used for the cationic and anionic selectivity experiments. 3-Mercaptopropionic acid (3-MPA, Sigma–Aldrich) and Tetramethylammonium hydroxide (TMAOH, Fluka 25% in water) were used without further purification. High purity water with a resistivity of 18 MΩ cm^{-1} was used throughout all the experiments.

2.2. Characterization techniques for the adsorbent system

SPION and nanoparticle composites (NPCs) synthesized by functionalization of SPION with 3-MPA were imaged with transmission electron microscopy (HR-FEG-TEM, JEOL JEM-2100, Tokyo, Japan). TEM–EDX for chemical composition determination was applied for the nanoparticles in dry form. The stability and the homogeneity of the SPION suspension in hydrodynamic mode were determined by dynamic light scattering (DLS, Delsa Nano C, Beckman Coulter, Brea, CA, USA). thermogravimetric analysis (TGA, Q5000, TA instruments, New Castle, DE, USA) was employed to measure the weight variation and determine if the particles were loaded with the reagent. Fourier transform infra-red (FTIR, Nicolet Instruments model Avatar-100 equipped with ATR diamond at 303 K, Madison, WI, USA) was used to verify the interaction between SPION, 3-MPA and their bonding before and after the adsorption process [20–22].

2.3. Synthesis of adsorbent materials

The synthesis procedure of SPION ($\sim$10 nm) and 3-MPA-coated SPION has been described elsewhere [23]. A stock solution of iron(III) in chloride medium was prepared by dissolving the salt with a deoxygenated 0.2 mol/L HCl aqueous solution. This solution was added to a deoxygenated solution of 0.7 mol/L NH_4OH under mechanical stirring. After a few minutes, the appropriate salt of iron(II) in 2:1 ratio was added to avoid the partial oxidation of Fe(II). The particles were aged in the solution for about 45 min under mechanical stirring and nitrogen bubbling, decanted by magnetic settling, and washed with deoxygenated water several times. A known amount of the synthesized particles was mixed with 3-MPA solution (150 mM) in toluene using a rotary shaker for 24 h. After phase separation using magnetic settlement, the particles were washed with toluene three times to remove the excess of 3-MPA deposited on the surface of the particles. The particles were dried at room temperature (23 °C). FT-IR was used to check whether the reagent was bound to the surface of the particles, in a wavenumber range 4000–600 cm^{-1} [24,25]. TGA analysis was carried out with heating rate of 10 °C/min in nitrogen until 900 °C [26,27].

2.4. Adsorption and desorption experiments

The adsorption experiments were performed by mixing a known amount of 3-MPA-coated SPION with aqueous solutions of As(V) in 0.2 M Acetic acid/Acetate medium using a rotary shaker at room temperature (23 °C). The pH of the solution was controlled using either HNO_3 or NaOH standardized solutions and confirmed by pH measurements (pH-meter, Crison, Barcelona, Spain). After mixing, the aqueous phase was separated from the solid phase by magnetic settlement and centrifugation at 14,000 rpm (Geno-fuge 16 M, Techne, Prinston, NJ, USA). The concentration of metal ions in the supernatant was determined by inductively coupled plasma atomic emission spectroscopy (ICP-AES, iCAP 6000, Thermo Fisher, Waltham, MA, USA). As(V) adsorption was calculated by mass balance and the effect of different parameters, such as time, pH and initial As(V) concentration were recorded. The dissolution of iron oxide was monitored by determining the concentration of iron in aqueous solutions.

In the desorption experiments, 10 mL of the elution solution (HNO_3 or NaCl) was added to an accurately-measured quantity of 3-MPA-coated SPION loaded with As(V). After 60 min of contact at temperature 23 °C, the aqueous and the solid phases were separated by centrifugation and the concentration of As(V) in the supernatant was measured.

The total adsorption capacity was expressed as mmol of Arsenate (or other metal in case of selectivity experiments) per gram of adsorbent system.

2.5. Selectivity experiments

Two different experiments were performed to study the selectivity of the adsorbent. In one, solutions of As(V) containing metal ions such as Cu(II), Ni(II) and Zn(II) in molar ratios 1:1 and 1:2 (As(V): metal ions) were treated in order to know if the adsorbent system can be used for As(V) removal in the presence of metals. In the other, solutions of As(V) containing 0.25 mol L^{-1} of Cl$^-$, NO$_3^-$, SO$_4^{2-}$ or PO$_4^{3-}$ (ratio 20:1 respect of As(V) total in solution) were treated to observe the behaviour of the absorbent system in the presence of interfering anions. The experiments were performed in the same way as the adsorption experiments by mixing a known amount of 3-MPA-coated SPION with the solutions using rotary shaker at room temperature (23 °C). The pH of the solution was controlled using either HNO_3 or NaOH standardized solutions and confirmed by pH measurements (pH-meter, Crison, Barcelona, Spain). After mixing, the aqueous phase was separated from the solid phase and the concentration of metal ions in the supernatant was determined by ICP-AES.

3. Results and discussion

3.1. Characterization of adsorbent material

The amount of 3-MPA coated on the surface of SPION was determined from the percentage mass loss measured by thermogravimetric analysis (TGA/DTG). As shown in Fig. 1, the TGA curve for SPION shows a mass loss over 100–350 °C of about 8%. This is most likely due to the loss of adsorbed water and dehydration of internal OH groups. However, for 3-MPA-coated SPION, the TGA curve shows two mass loss steps. The first mass loss step over 100–180 °C might be due to the loss of residual water adsorbed physically in the sample. The second mass loss over 200–800 °C was due to the decomposition of 3-MPA. Based on the TGA data, the amount of 3-MPA coated on the surface of SPION is determined to be 3.7 mmol/g.

The TEM image of 3-MPA-coated SPION is shown in Fig. 2a. A review of the actual existing literature highlights an optimal particle size range between 8–20 nm for adsorption applications. As it can be observed, the main nanoparticle size obtained by using the described synthesis method has an average size about 15–20 nm [28–30]. Energy Dispersive X-ray (EDX) analysis data (Fig. 2b) show that the main compositions of the sample are Fe, O, and S. The presence of sulphur in the sample is a confirmation of the coating process [31,32].

In order to confirm the coating of the SPION surface with 3-MPA, FT-IR spectrum of SPION, 3-MPA-coated SPION, and 3-MPA